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ABSTRACT

We have investigated phase behaviors of a series of polyphenylacetylene derivatives, poly[di(*n*-alkyl) ethynylterephthalates] (**Pn**, *n* is the number of carbon atoms of *n*-alkyl group, from 2 to 14), which are largely influenced by the length of *n*-alkyl tails on 2,5-position of the phenyl group. With short alkyl groups ($n \le 6$), **Pn**s form columnar liquid crystalline (Col) phases due to the "jacketing effect" of sidechains. As the alkyl tails become longer ($n \ge 8$), an isotropic phase, which can be considered as a reentrant one (I_{re}), is identified between lamellar phase (Lam) at low temperatures and Col phase at high temperatures. This unusual phase behavior is determined by the motional state of the side-chains. Thanks to in-situ variable temperature solid-state NMR experiments, the motion of main- and sidechains in different phases were distinguished, providing strong evidence for the entropy effect of sidechains which drives I_{re} and then Col phase in **Pn**s ($n \ge 8$) upon heating.

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1. Introduction

In the past decades, liquid crystalline (LC) polymers have attracted considerable attention due to their feasibility of chemical modification, melt processability, and response to different external fields [1]. Side-chain liquid crystalline polymers (SCLCPs) can be readily obtained by attaching anisotropic mesogens to the backbone via a flexible spacer [2]. Phase structures of SCLCPs, such as nematic (N), smectic A (S_A), smectic C (S_C), and columnar (Col) phases, are largely determined by the nature of the mesogenic groups of SCLCPs [3]. Phase transition of SCLCPs is of key importance not only from the view of fundamental research, but also as regard to their promising applications in liquid crystalline elastomers [4] and shape memory materials [5,6].

Generally, phase transition of SCLCP takes place from a less ordered phase at high temperatures to a phase with ordered structure at lower temperatures [7]. However, similar to those exceptions in some low molecular weight LC compounds, an unexpected reentrant nematic phase (Nre) was discovered in polyacrylates containing cyano mesogenic units [8] and binary copolymers of 4'-(ω vinyloxyalkoxy)biphenyl-4-yl cyanides [9]. Neutron scattering and X-ray diffraction experiments clearly demonstrated that the conformation of the backbone changed in the Nre phase upon approaching the S_A [10,11]. Recent studies showed an isotropic phase (Iso) "reentry" in mesogen-jacketed LC polymers (MJLCPs), which are a special kind of SCLCP with bulky mesogenic groups laterally attached to the polymer backbone via a short linkage or a single carbon-carbon bond [12,13]. Basically, the strong steric interaction between the main- and side-chain of MJLCP makes the whole macromolecule a rod-like unit to form Col phases [14–16], which are usually stable at high temperatures until thermal decomposition. However, Col phases in some of poly[di(alkyl) vinylterephthalates] (PDAVT) [17] and poly{2,5-bis[(4butoxyphenyl)oxycarbonyl]styrene} [18] disappeared upon





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cooling and an Iso phase could be found at lower temperatures. Study of poly{2,5-bis[(4-alkoxyphenyl)oxycarbonyl]styrene} (P-OCm, *m* is the number of carbon atoms of the alkoxy group, m = 1-18) revealed that LC behaviors of P-OCm depended on the alkoxy groups [19]. Namely, P-OCm (m = 1, 2) showed only a stable Col phase; P-OCm (m = 4-8) presented an Iso and a Col phase at low and high temperatures, respectively; P-OCm (m = 10-18) exhibited an Iso phase which separated S_A at low temperatures and Col at high temperatures. Assuming there is a transition of Col-Iso at sufficiently high temperatures (virtual one, above the decomposition temperature) for MJLCP, the Iso phase at lower temperatures can be considered as a reentrant one (I_{re}) . It is argued that a gain of conformational entropy of the system is favorable for the transformation of I_{re} to Col upon heating. However, there is so far hardly any experimental work to discuss the possible entropy effect of this unique phase transition [18,19].

In this work, we investigate a series of polyphenylacetylene derivatives, poly[di(n-alkyl)] ethynylterephthalates] (**Pn**, n is the number of carbon atoms of alkyl group, n = 2-14, see Scheme 1), attempting to provide deep insight on the multiple phase transitions with Ire phase. Apparently, the molecular design of **Pn** bearing a polyacetylene backbone has a root in PDAVT with similar side chains [17]. Our previous work demonstrates that PDAVT with alkyl groups ranging from propyl/isopropyl to hexyl can form a longrange-ordered hexagonal Col phase (Col_h). In the Col_h phase, PDAVT chain behaves like a core-shell cylinder, wherein the mainchain (core) is surrounded by alkyl tails (shell). When alkyl groups became longer, the Col phase of PDAVT is formed partially, coexisting with the disordered phase. In the case of dodecyl, PDAVT becomes completely disordered. Here, for **Pn**, the conformation and dynamic of semi-rigid polyacetylene backbone are greatly distinguished from those of the flexible main-chains and sidegroups [20–22], enabling us to investigate directly the entropy effect of the side-chain during the phase transition. As shown by the results of differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD) methods, phase behaviors of **Pn** are largely influenced by the length of sidechains. While **Pn**s with $n \le 6$ are in Col phases, **Pn**s $(n \ge 8)$ undergo an unusual phase transition of lamellar-I_{re}-Col phase with increasing temperature. Besides a thermodynamic interpretation, we also investigated the molecular dynamic of the main-chain and side-chains using solid state NMR, which sheds light on the sidechain effect on the phase transition.

2. Results

2.1. Polymer synthesis and characterization

Scheme 1 gives the synthetic route of the monomers (**Mn**) and polymers (**Pn**). Details of synthesis and characterization of **Mn** and **Pn** are provided in the Supporting Information (SI).

Polymerizations of **Mn** were carried out under mild condition using the zwitterionic organorhodium complex of [Rh(nbd) $B(C_6H_5)_4$] as the catalyst [23]. Dark brown polymers (**Pn**) were obtained with high molecular weight and moderate yield (Table 1).

Table 1	
Polymerization	results of Pns.

Polymer ^a	M _w (g/mol) ^b	$M_{\rm w}/M_{\rm n}^{\ b}$	Yield (%)	$T_{g} (^{\circ}C)^{c}$
P2	81 000	1.8	33.8	58
Р3	115 000	1.7	73.3	13
P4	118 000	1.6	70.9	-11
P5	100 000	2.4	66.4	-22
P6	108 000	2.1	63.4	-30
P8	101 000	1.6	64.9	_d
P10	100 000	1.5	77.5	_d
P12	130 000	1.6	86.9	_d
P14	46 000	1.9	50.4	_d

^a Polymerization was carried out in tetrahydrofuran (THF) using [Rh(nbd) $B(C_6H_5)_4$] as the catalyst at 30 °C under nitrogen for 24 h; [monomer] = 0.2 M, [catalyst] = 2 mM.

^b Estimated by GPC in THF on the basis of a polystyrene calibration.

 $^{\rm c}\,$ Determined from DSC curves in the second heating process (heating rate 20 $^{\circ}\text{C}/$ min).

^d Not determined.



Scheme 1. Synthesis route of the monomers and polymers.



Fig. 1. 1 H NMR spectrum of **M6** and **P6**. The solvent (CDCl₃) peak is notified by the asterisk.

As shown by the ¹H NMR result (Fig. 1), the newly formed olefin proton in **P6** is observed at δ 5.8–4.8 ppm as a broad peak, indicating a *cis* rich configuration of the main-chain [21]. The assigned *cis*-content of **Pn**s by ¹H NMR spectra [24,25] is 60–70% (Fig. S1). Note that the chemical shift appears at higher field compared with the typical *cis* olefin proton at δ 6.5–5.6 ppm, indicating that the olefin proton is significantly shielded by the phenyl ring. The broad peak may result from irregular configurations (e.g. head-to-head or head-to-tail) and stiff polyacetylene backbone [26].

2.2. Overall phase behaviors of Pns

Presented in Fig. 2 are POM images of **Pn**s. Schlieren textures of **P2**, **P4**, and **P6** imply a phase with nematic feature. As shown by Fig. 2b of **P3**, a banded texture can be obtained after the samples were mechanically sheared, similar to those formed under an external shear field in low ordered LC phases and two-dimensional (2D) Col phase [14,18,27,28]. When the alkyl chain becomes longer, such as **P8** and **P10**, the samples are sticky enough to be readily pressed between two slide glasses, exhibiting flower-shaped textures (Fig. 2f and g). The birefringence of **P12** and **P14** (Fig. 2h) at room temperature is rather weak and the texture is atypical.

DSC measurement of **Pn**s verified that there was a critical length of the side chain around n = 8 where phase behaviors of **Pn**s were markedly altered (see Fig. S2 in SI). **Pn**s with short alkyl chains (n = 2-6) only exhibit glass transitions during heating. The glass transition temperatures (T_{gS}) are 58, 13, -11, -22, and -30 °C as n increases from 2 to 6 (Table 1). For **Pn**s with longer tails (n = 8-14), multiple transitions can be inferred by the broad endothermic peaks at temperatures around or below room temperature.

One-dimensional (1D) XRD experiment at room temperature confirmed the critical side-chain length of around n = 8. As shown in Fig. 3, **Pn**s exhibit sharp diffractions at low angles and amorphous halos at wide angles, evidencing the existence of ordered LC structures. For $n \le 6$, the diffraction peaks gradually shift to lower angles as n increases. However, for n = 8 and 10, the low angle peak is only partially formed with scattering halo underneath, suggesting that the LC phase coexists with a large amount of amorphous part in the samples. When n increases to 12 and 14, the diffractions shift greatly to lower angles and weak peaks appear in the wide angle region (2θ around 20°). The decreased intensity and discontinuous shift of the peak position caused by increasing n imply that phase structures of **Pn**s are significantly affected by the length of alkyl tails. In the light of the above results, we will discuss phase structures of **Pn**s for $n \le 6$ and $n \ge 8$, respectively.



Fig. 2. LC textures of P2 (a), sheared P3 (b), P4 (c), P5 (d), P6 (e), P8 (f), P10 (g), and P14 (h). The pictures of (b)–(e) were captured at room temperature, while those of P2, P8, and P10 were observed at 70 °C. Scale bars: 50 µm (a) and 100 µm (b–h).



Fig. 3. 1D XRD patterns of Pns at room temperature.

2.3. Phase behavior of Pn with $n \leq 6$

Taking P6 as an example, the representative 2D XRD patterns of this class of **Pn** are shown in Fig. 4. The sample could be easily oriented by mechanical shearing at room temperature. Although P6 possesses a rather low T_g of -30 °C, its uniaxial orientation can be well retained after shearing (Fig. 4a), which can be attributed to the semi-rigid main-chain. As shown by Fig. 4b, with the X-ray beam parallel to the shear direction, the low angle diffraction demonstrates a six-fold symmetry, indicating a hexagonal structure. As there is no higher order diffraction detected, we can identify that **P6** forms a hexagonal Col nematic phase [15]. The d-spacing (d_{10}) of the low angle diffraction, i.e., the (10) diffraction of hexagonal lattice, is 1.56 nm. With such a phase structure similar to that of MJLCPs [15,17], the building block for the Col phase is the cylinderlike macromolecules. Thermal 1D XRD experiments show that the Col phase can be maintained below T_g during cooling (Fig. 4c), and its diffraction intensity is enhanced in the heating process (Fig. 4d).

Similarly, P2, P3, P4, and P5 also form Col phase, of which the

values of d_{10} are 1.23, 1.29, 1.37, and 1.51 nm, respectively. As shown in Fig. 5a (black square), the d_{10} increases smoothly with the length of alkyl tails from **P2** to **P6**. In terms of the unit cell parameter *D* of hexagonal lattice ($D = 2d_{10}/\sqrt{3}$), a linear dependence of D^2 on *n* can be fitted (Fig. 5b), confirming that **Pn**s ($n \le 6$) exhibit the same Col phase.

2.4. Phase behavior of Pn with $n \ge 8$

For **Pn**s with longer alkyl chains, it is found that the overlapped transitions shown in Fig. S2 can be clearly resolved in the cooling process at a reduced rate of 2 °C/min (see Fig. 6a for **P12**). A very weak exothermic process is observed at the temperatures ranging from 24 to 16 °C, followed by an exotherm extended to around -45 °C. The 1D XRD results of **P12** during the cooling and heating processes are presented in Fig. 6b and c, respectively. Obviously, the low angle diffraction peak changes position upon cooling, locating at $q_1 = 3.09 \text{ nm}^{-1}$ ($q = 4\pi \sin\theta/\lambda$) at high temperatures and at $q_2 = 1.92 \text{ nm}^{-1}$ at low temperatures. Accordingly, the cooling process can be divided into three stages.

First, at high temperatures ($T \ge 30 \,^{\circ}$ C), the sharp diffraction with $q_1 = 3.09 \text{ nm}^{-1}$ corresponds to *d*-spacing of 2.03 nm, close to that of P6 (1.56 nm). We consider that P12 forms the Col phase structure similar to **P6**, as the corresponding D^2 (D = 2.34 nm) falls on the fitted line of $D^2 \sim n$ for the Col phase (Fig. 5b). This diffraction peak coexists with a halo, meaning that the Col phase is partially developed in the sample. Second, the diffraction intensity reduces as the temperature decreases. A broad halo is observed at intermediated temperatures (20-10 °C), suggesting an isotropic state of P12. The transition from Col to Iso phase is also evidenced by the weak exothermal peak of 24–16 °C on the DSC cooling curve. The Iso phase can be assigned as a reentrant one (Ire), as it follows the Col phase upon cooling, similar to those observed in MJLCPs recently [13,18,19]. Third, a new diffraction with $q_2 = 1.92$ nm⁻¹ appears at temperatures lower than 10 °C, of which the *d*-spacing is 3.27 nm, comparable to length of the stretched side-chain with the two tails extending to opposite directions. We presume that P12 forms a lamellar (Lam) phase at low temperatures, although the higher order diffractions are missed. Formation of Lam phase should be related with the crystalline tendency of alkyl chains at



Fig. 4. 2D XRD patterns of P6 film sheared at room temperature obtained with the X-ray beam perpendicular (a) and parallel (b) to the shear direction. The arrow (yellow) in (a) indicates the shear direction. 1D XRD profiles of **P6** recorded during the cooling (c) and heating (d) process. Typical temperatures during the measurements are listed in (c) and (d).



Fig. 5. Relationship between phase structures of **Pn**s and their alkyl chain length *n*. (a) Summary of *d*-spacing of the first order diffraction of **Pn**s in Col (black square) and Lam (red triangle) phases. The dependence of *d*-spacing on *n* in Lam phase for **Pn** ($n \ge 8$) can be fitted with the red linear line. (b) Relationship between the hexagonal unit cell parameter *D* and *n* for **Pn**s in Col phase. The fitted red line suggests that D^2 is proportional to *n*.



Fig. 6. DSC cooling curve recorded at 2 °C/min (a) and 1D XRD profiles of **P12** recorded during the cooling (b) and subsequent heating (c) process. Note that the weak exothermal peak in (a) between 24 and 16 °C corresponds to the transition of Col to I_{re} phase. Typical temperatures during the measurements are listed in (b) and (c).

lower temperatures (see the weak peak at ~0.40 nm of **P12** in the XRD profile in Fig. 3). XRD results indicate that P12 possesses an unusual Col-I_{re}-Lam transition, which is further verified by POM experiment (Fig. S3). The birefringence of **P12** disappeared when cooling to 28 °C, reappeared at 7 °C, and became brighter at lower temperatures. Heating experiment of **P12** demonstrates that the transition is reversible (see Fig. 6c).

Systematic experiments of **P8**, **P10**, and **P14** (Figs. S4, S5, and S6 in SI) proved that **Pn**s with long alkyl tails shared the similar phase transition behavior, of which the transition temperatures became lower when the alkyl tail length is reduced.

3. Discussion

3.1. Phase diagram of polymers

The overall picture of the phase behaviors of **Pn**s as functions of n is summarized in Fig. 7. At high temperatures (below the isomerization temperature of polyacetylene backbone), all **Pn**s can form Col phases. Upon cooling, phase structures of **Pn**s strongly depend on the length of alkyl tails. For **Pn**s of $n \le 6$, they enter into the glass state (G) with the Col phase maintained, and the T_g is greatly reduced by increasing n. For $n \ge 8$, **Pn**s undergo unusual phase transition of Col-I_{re}-Lam. The transition temperatures increase as n



Fig. 7. Phase diagram of **Pn**s. Col, columnar; G, glass state; I_{re} , reentrant isotropic; Lam, lamellar. Transition temperatures are obtained on the cooling process except that the T_{re} s are read from the heating DSC curves. Dot lines are used to guide the eyes.

increases from 8 to 14. In the following we will discuss the quantitative relation between the phase structure dimension and *n*.

First, for the Col phase at higher temperature, using the data of *D* of all the samples with $n \le 6$ and ≥ 8 , the relationship between D^2 and *n* can be well fitted as $D^2 = 1.17 + 0.36n$ (Fig. 5b). Thus, the

microphase-segregated model in the supramolecular column of Col phase can be inferred, where the polyphenylacetylene main-chain locates in the core of the column and the alkyl chains are disordered outside [16,29]. The diameter of the main-chain can be estimated to be 1.08 nm in the case of n = 0.

Second, *d*-spacing of the Lam phase of **Pn** ($n \ge 8$), which are of 2.00, 2.60, 3.27, and 3.71 nm, increases with increased *n*. Linear fitness (Fig. 5a) shows that the increment of layer thickness is of ~2.7 Å for each increment of *n*, comparable of twice of the theoretic value of 1.27 Å for one methylene unit [30,31]. It means that Lam phase may take a double layer structure, where the stretched side chains are parallel to each other without interdigitation.

3.2. Multiple effects of alkyl tails on phase behavior of Pn

It is interesting to find that, compared to the prototype polymer of polyphenylacetylene, **Pn**s with alkyl tails attached to 2,5position of the phenyl group have thoroughly changed phase behaviors. Considering the di(alkyl) terephthalate moiety as a whole, the bulky pendant groups can impose the "jacketing effect" on the polyacetylene backbone. As a result, the *cis*-rich backbone of **Pn** adopts a stretched *cis*-transoidal conformation [32]. For such a semi-rigid main-chain, the alkyl tails can be regarded as bound solvent, similar to that in hairy-rod polymers [33,34]. The covalently bonded alkyl tails not only act as plasticizers to greatly reduce the T_g , but also contribute to the conformational degrees of freedom to improve the mobility of the semi-rigid macromolecules. We propose that the packing behavior and motion of side chains, which vary with the tail length and the temperature, play a significant role on the phase evolution of **Pn**s.

With the pronounced "jacketing effect" of side chains, all the **Pn**s studied can form Col phases, which take the supramolecular columns as building blocks. It is worth to note that at higher temperatures the Col phase is better developed. As shown in Fig. 4, the diffraction intensity of P6 increases with increased temperature. This outcome suggests that the electron density contrast between the core (main-chain) and the shell (alkyl tails) in the microphase-segregated supramolecular column is improved. For the samples with $n \ge 8$, the Col phase can only be observed once the temperature becomes sufficiently high. The enhanced microphase separation within the supramolecular column and/or the appearance of Col phase at high temperatures clearly indicates that the Col phase formation of **Pn** relies on the mobility of alkyl tails. As the liquid-like alkyl tails bonded to the semi-rigid main-chain seek more conformations in space and maximize their conformational entropy with increased temperature, the Col phase of **Pn** becomes an efficient packing scheme. In other words, the stronger "jacketing effect" of side-chains on main-chains at higher temperatures, which can result in the Col phase, originates from entropy gain of the alkyl tails.

Interestingly, the Col phase of **Pn**s with $n \le 6$ is stable during the entire temperature range $(-50-80 \ ^{\circ}C)$, while for PDAVT the Col phase of n = 6 disappeared at room temperature [17]. This difference is related to the rigidity of backbones. For the semi-rigid polyacetylene main-chain of **Pn**s with the *cis*-transoidal conformation, its conformation takes a little change during the cooling process. As the movement of short alkyl chains slows down below T_{g} , the Col phase becomes frozen in the glassy state and the diffraction intensity reduced during cooling (Fig. 4). One can anticipate that the Col phase should collapse eventually when the glass transition occurred at a sufficiently low temperature. Such a transition is observed in **Pn**s with longer alkyl chains ($n \ge 8$) and other MJLCPs, such as PDAVT ($n \ge 6$) [17] and P-OCm (m = 4-18, m is the number of carbon atoms of the alkoxy group) [19]. Indeed, the T_{gs} of these polymers are much lower than the Col-I_{re} transition

temperatures.

From the view of chemical structure, **Pn**, PDAVT and P-OC*m* have a similarity, i.e., the I_{re} phase appears only when the length of alkyl tails achieves a critical value. As mentioned before, the long alkyl chains bound to the semi-rigid main-chains behave more likely as "solvent". Different volume fractions of the "solvent" determine the distinct phase behaviors of **Pn**s with short and long alkyl chains. According to Onsager's theory on the isotropic to nematic phase transition [35], the volume fraction of the rigid component should be high enough to form ordered LC phase. For **Pn**s with short alkyl tails, the volume fractions of the "solvent" are relatively small, more favorable for the Col phase. While the volume fraction of alkyl tails ("solvent") is increased, the main-chains become "diluted" in the system. We consider that the "dilution" effect shall be tightly related to the formation of I_{re} phase in **Pn**s ($n \ge 8$).

As is well known, long alkyl tails tend to take stretched conformations to form ordered packing with each other, which usually occurs at temperatures close to the crystallization temperatures of alkyl groups. Due to this crystallization tendency, Lam phase formation can be expected for **Pn** with long alkyl tails at low temperatures, which is an enthalpy driven process. As determined by XRD results of the Lam phase, the stretched side-chains form a double layer structure, similar to that reported for hairy-rod polymers with high graft density of side-chains [36]. According to DSC results of **Pn**s of n > 8, the transition temperatures for Lam phases are 10-15 °C higher than the crystallization temperatures of alkanes (C_nH_{2n+2}) bearing the same numbers of carbon atoms [19]. This may be ascribed to the microphase separation between mainand side-chains of **Pn**s, which facilitates the side-chain ordering. The alkyl chain length determines not only the transition temperature of the Lam phase, but also the ordered degree of this phase. For example, the onset temperature of the Lam phase for P14 is the highest among the samples (~30 °C) and the diffraction peak becomes well-defined at 20 °C upon cooling (Fig. S6).

Based on the above arguments, we consider that the "jacketing effect" and the crystallization tendency of the side-chains, which are entropic and enthalpic in nature, respectively, dominate the phase structures at high and low temperatures. The I_{re} phase at intermediate temperatures should be a result of the balance between the conformational entropy of side-chains and the main-chain/side-chain interaction. For **Pn** of $n \ge 8$, the temperature window of the I_{re} phase can be quite narrow, especially for **P12** and **P14** during the heating process. As shown in **P12** upon heating from 20 to 40 °C (Fig. 6c), there is coexistence of two phases at specific temperatures: Lam-I_{re} at 20–35 °C, and I_{re}-Col at higher temperatures, suggesting a competitive transformation among the three phases.

3.3. Componential dynamics determined by solid state NMR

In the above discussion, we have mentioned that the conformational entropy gain of the side-chains is responsible for the formation of the Col phase. In the following, we employ in-situ variable-temperature solid state NMR techniques to study the dynamics of the heterogeneous components (main-chain and sidechain) in different phases. 2D ¹H-¹³C wideline separation (WISE) NMR experiment is a powerful tool for the determination of heterogeneous dynamics in solid polymers, which is useful for the characterization of polymers including both hard and soft components [37,38]. The observed ¹³C chemical shifts indicate segmental compositions of the components. On the other hand, it is wellknown that the line width of the ¹H line reflects the nature of the dipolar interaction between the protons and thus can be exploited to monitor the dynamic behavior of polymer chains. Therefore, different componential dynamics can be distinguished by the ¹H wide-line spectrum, broad if rigid and narrow if mobile [39].

We carried out 2D WISE NMR experiments for **P12** at four temperatures of -20, -10, 28, and 36 °C, covering the transition of Lam - I_{re} - Col phase. Typical 2D ¹H $^{-13}$ C WISE spectrum of **P12** at 28 °C is shown in Fig. 8a as an example. The chemical shifts indicate three components in the polymer, i.e., phenyl group (131.4 ppm), $-OCH_2-$ (66.0 ppm), and the alkyl tails (33.3 ppm), which are marked by the number of 3, 2, and 1, respectively. It should be noted that the chemical shift of *cis*-double bond of polyacetylene mainchain (at about 140 ppm) cannot be identified due to the poor signal. However, the mobility of the main-chain can be inferred from the results presented by the phenyl groups which are directly attached to the semi-rigid backbone.

The slice projections of the phenyl group, $-OCH_2-$, and alkyl tails at the selected temperatures are presented in Figs. 8b, c, and 8d, respectively. At low temperatures of -20 and -10 °C, the phenyl and $-OCH_2-$ groups exhibit broad lines, indicating that these groups (involving the main-chains) are rigid components in the polymer. Aliphatic groups are less rigid in the Lam phase, as shown by relatively narrow lines. As the temperature increases to 28 and 36 °C, where the system enters into I_{re} and Col phase later, a strong and sharp peak is observed for the aliphatic groups, indicating that the flexible alkyl tails become remarkably mobile. On the other hand, the line width of phenyl exhibits a little increase. It is noticeable that at 36 °C there is a rather broad halo (line width of



Fig. 8. 2D ¹H–¹³C WISE spectrum of **P12** at 28 °C (a). In the ¹³C dimension (top), the chemical shifts of phenyl group, $-OCH_2$ -, and carbons of the alkyl tails are marked by the number of 3, 2, and 1, respectively. ¹H wide-line spectrum (slice projections) of different components at the selected temperatures are shown as (b) phenyl groups at 131.4 ppm, (c) $-OCH_2$ - at 66.0 ppm, and (d) carbons of the alkyl tails at 33.3 ppm.

55 kHz) at the bottom of the peak. Such a broad line width is typically seen in the rigid solid, i.e., polystyrene at glassy state. For -OCH₂- groups, a small narrow line clearly appears at the peak center at 28 °C, and the peak is slightly narrowed at 36 °C after P12 enters Col phase. From this observation, we can infer three types of motional behaviors: 1) the phenyl groups linked to the polyacetylene backbone remain to be rigid with increased temperatures: 2) part of the ester groups on the 2.5-position of phenyl become more mobile upon heating; and 3) alkyl tail move quickly as disordered liquid after the Lam phase is melted. Consequently, we consider that the mobility of side chains is the key factor associated with the unusual phase transition of **Pn**s with long alkyl groups. The conformational entropy of the side-chains is maximized in the Col phase, although the transitional movement of the main-chains is restricted in some degree. The WISE experiments strongly support the idea that the driving force of the Col phase in this series of polymer is the conformational entropy gain of the side-chains.

4. Conclusions

In summary, we have investigated the side-chain effect on phase behaviors for a series of polyphenylacetylene derivatives **Pn**s. Bearing *n*-alkyl tails on 2,5-position of the phenyl group, the sidechains can provide considerable "jacketing effect" to the backbone of **Pn**, leading to the Col phase as usually observed in MILCPs. **Pn**s with longer alkyl groups ($n \ge 8$) exhibit complex phase transitions. Due to the differences in both the chemical structure and rigidity of the main- and side-chains, microphase separation between mainchain and side-chains of **Pn**s $(n \ge 8)$ is achieved both in the Col phase and the Lam phase. In the Col phase at high temperature, alkyl tails behave like disordered liquid paraffin, of which the entropy is maximized. On the other hand, the motion of the sidechains is largely frozen but still independent of the main-chain at low temperatures, and the tendency of parallel arrangement favors for the Lam phase. The "solvent" nature of the alkyl chains is strongly supported by the Ire in the intermediate temperature region, which provides the pathway for the whole macromolecule to adjust its conformation and packing behaviors. It should mention that, it is still an open question whether the conformation and arrangement of main-chains plays a role in phase behaviors of **Pn**s, although we emphasize that the packing and motion state of alkyl tails are the key factors. Nevertheless, the solid state NMR results prove the dynamic heterogeneity of the main- and side-chains in different phases. The fast motion of alkyl tails at high temperatures supports that the Col phase of **Pn** is entropy-driven, which can also be the origin for Col phases observed in other MJLCPs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.02.012.

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